Critical Review

Environmental Chemistry of Aminopolycarboxylate Chelating Agents

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Aminopolycarboxylate chelating agents are under scrutiny due to their influence on metal availability and mobility and in particular due to their persistence in the environment. In this review chelate adsorption, metal-mobilization, metal-exchange, mineral dissolution, reactive transport, photodegradation, and chemical degradation are all shown to be substantially affected by the chelated metal ion. The different reactivities of the metal-complexes have to be considered when assessing the reactions of chelating agents in the environment because they occur in natural waters predominantly in the form of metal complexes. Knowing the speciation of chelating agents in natural waters is therefore crucial for predicting their environmental fate. Despite this importance, only a few speciation measurements have been reported for natural waters, and model calculations have been frequently used instead. These calculations are, however, complicated by slow metal-exchange reactions that result in a nonequilibrium speciation and by the presence of naturally occurring ligands that compete with the chelating agents for available metals. The basis for a refined risk assessment of aminocarboxylate chelates should be the actual speciation in the natural water directly determined by analytical methods. The discussion of the influence of chelates on metal availability and fate also has to include the potential presence of other aminopolycarboxylate chelating agents besides the well-known EDTA and NTA.

Introduction

The environmental fate of chelating agents has received considerable attention. EDTA (ethylenediaminetetraacetic acid) for example occurs at a higher concentration in river water than any other identified organic compound (*1*, *2*). Chelating agents have the potential to perturb the natural speciation of metals and to influence metal bioavailability (*3*, *4*), and their presence may lead to the remobilization of metals from sediments and aquifers, consequently posing a risk to groundwater and drinking water (*5*, *6*). The largest concern, however, is that many chelating agents (e.g. EDTA) are not biodegradable and are therefore persistent in the environment (*7*, *8*).

Strong chelating agents occur in natural waters predominantly in the form of metal complexes. A discussion of the fate of a chelating agent always has to address the presence of metals and how they interact with the chelates. There are many studies emphasizing the importance of chelation on *metal* bioavailability, plant uptake, toxicity, transport, adsorption, distribution, and fate (*9*). Conversely, *chelating agents* are also affected by the presence of metals resulting in different reactivities of metal-chelates.

Environmental concentrations, usage, biodegradation, and toxicology of chelating agents have already been thoroughly reviewed (*3*, *7*, *8*, *10*−*16*) and shall therefore not be discussed again here. What is missing, however, is a critical evaluation of the chemistry of chelates in natural waters. This review will present an overview of the environmental chemistry of anthropogenic chelating agents of the group of the aminopolycarboxylates, in particular of EDTA and NTA (nitrilotriacetic acid). Where available, data from other aminopolycarboxylates such as DTPA (diethylenetriaminepentaacetic acid) and EDDS (ethylenediaminedisuccinic acid) are also included, but the literature about the environmental chemistry of these compounds is very sparse.

This review covers exchange reactions (metal-exchange in solution, adsorption to mineral surfaces, dissolution of minerals, and remobilization of adsorbed metals), redox reactions involving the coordinated metal ion, reactive transport, degradation (photodegradation and oxidation), and the determination of their speciation by analytical techniques and speciation calculations. The available data are reviewed with respect to the importance of speciation on the reactivity of chelating agents.

Exchange Reactions

Metal Exchange. The equilibrium speciation in a metal−ligand system is controlled by the concentrations of all metals and ligands and the stability constants of all complexes, and if another metal−ligand complex or metal ion is added to the solution a new equilibrium will be attained. This knowledge, however, is only of limited value if the kinetics of the reaction are not considered. Coordination reactions of metal ions with ligands containing multiple bonding groups such as EDTA are often kinetically hindered (*17*). The exchange reactions of Fe(III)EDTA are notably slow (*18*). Fe(III)EDTA is an important EDTA species released from wastewater treatment plants and comprises 20−90% of total EDTA in the effluents (*19*). The very high stability constant for the Fe(III)EDTA complex (logK of 27.2, (*20*)) is only of limited significance for predicting the speciation in a natural system containing other cations since the metal ion that captures the greatest amount of ligand at equilibrium depends on the product of K multiplied by the concentration of the free metal ion. In the case of Fe(III)EDTA, the free Fe^{3+} concentration at neutral pH is very low due to the insolubility of iron oxides, and, therefore, other cations such as Ca or Zn can outcompete Fe(III). Fe(III)EDTA is, therefore, not stable in a natural water at $pH > 7$ in the presence of other metalions such as Zn due to competitive complexation of EDTA by Zn.

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$$\mathrm{Fe(III)EDTA^{-} + Zn^{2+} \Rightarrow ZnEDTA^{2-} + Fe^{3+}_{(precipitated)}} \quad (1)$$

Fe(III)EDTA is observed in river water because Fe(III)EDTA has a half-life of about 20 days due to the slow exchange with Zn (*21*). The rate of complexation may also be strongly decreased by binding with Ca and Mg in hard waters (22, *23*). These observations indicate that reequilibration of a natural system undergoing perturbations of metal or ligand concentration cannot be assumed to be rapid without detailed knowledge about the exchange kinetics of the involved species. Equilibrium between EDTA and trace metals may therefore not be reached within the time scale of river flow, and Fe(III)EDTA and other species may be present although not predicted by equilibrium calculations.

Adsorption. Chelating agents have been developed to solubilize metals and keep them in solution. Therefore, it might be reasonable to assume that chelating agents decrease heavy metal adsorption by forming dissolved complexes. This, however, is only true for the very high concentrations of chelating agents used in technical applications. At low concentrations, chelating agents are able not only to decrease but also can significantly increase metal adsorption onto mineral surfaces (*24*). This is because chelates themselves are adsorbed onto surfaces. The reaction can be described by a ligand-exchange reaction similar to complex formation in solution

$$\equiv\mathrm{XOH} + \mathrm{L}^{n-} \Rightarrow \equiv\mathrm{XL}^{(n-1)-} + \mathrm{OH}^{-} \quad (2)$$

where $\equiv$XOH represents a surface site, e.g. on an iron oxide, and L is the added chelating agent. The formation of nonsorbing aqueous complexes or direct competition for surface sites can decrease metal adsorption. Ligands can increase metal adsorption through changes in the electrostatic properties of the solid/solution interface (*25*) or through sorption of the metal–ligand complex on the surface under formation of two different ternary surface complexes (*26*):

$$\equiv\mathrm{XOH} + \mathrm{ML}^{n-} \Rightarrow \equiv\mathrm{XO\text{-}M\text{-}L}^{(n+1)-} + \mathrm{H}^{+} \quad \text{(type A ternary surface complex)} \quad (3)$$

$$\equiv\mathrm{XOH} + \mathrm{ML}^{n-} \Rightarrow \equiv\mathrm{X\text{-}L\text{-}M}^{(n-1)-} + \mathrm{OH}^{-} \quad \text{(type B ternary surface complex)} \quad (4)$$

In type A ternary surface complexes the metal forms a bridge between the surface and the ligand, and in a type B ternary surface complex the ligand forms a bridge between the surface and the metal cation. Formation of type B ternary surface complexes completely changes the adsorption behavior of a metal. A metal shows in general increasing adsorption with increasing pH, while a type B ternary surface complex shows decreasing adsorption with increasing pH (Figure 1). Chelates are therefore able to *immobilize* metals through adsorption of the chelate complex, especially at low pH. Adsorption of chelate complexes has been almost exclusively modeled by type B surface complexes, i.e., assuming that the chelating agent bridges between surface and metal. Only Vohra and Davis (*27, 28*) have considered a type A metal-like surface complex to explain PbEDTA and PbNTA adsorption at low pH. Adsorption of uncomplexed Pb, however, is negligible at low pH, and, therefore, a metal-like surface complex is not very feasible. Consequently they later abandoned this approach and modeled metal–EDTA and metal–NTA adsorption using type B ternary complexes (*29*).

There is still a debate whether metal–EDTA adsorption onto oxide surfaces occurs by an outer-sphere or inner-sphere mechanism. Surface complexation models have assumed both inner-sphere (*31–33*) and outer-sphere complexes (*34*) to simulate experimental data. EXAFS measurements have also been interpreted by both inner-sphere complexation for ZnEDTA adsorption on goethite (*35*) and outer-sphere complexation for PbEDTA on goethite (*36*).

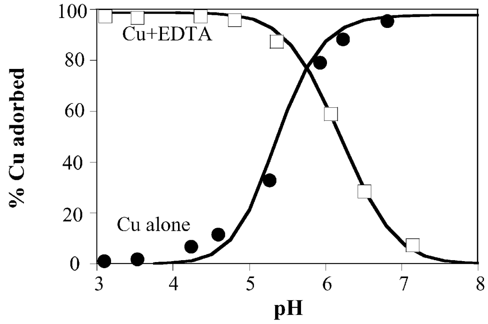

FIGURE 1. The presence of a chelating agent completely changes the adsorption behavior of a metal ion. The graph shows the adsorption of Cu and CuEDTA onto hydrous ferric oxide as a function of pH. The curves represent the model calculations. Data taken from ref *30*. Conditions: 10 μM CuEDTA or Cu, 1 mM HFO, 0.01 M NaNO$_3$.

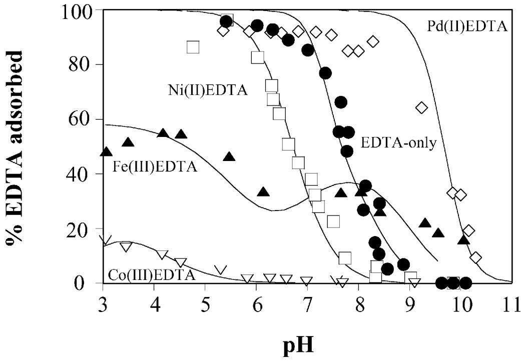

FIGURE 2. The adsorption of a chelate is modified by the complexed metal ion. The graph shows adsorption of free EDTA and of different metal–EDTA complexes onto goethite as a function of pH. The lines represent model calculations. Data taken from refs *31* and *41*. Conditions: 0.46 μM EDTA or metal–EDTA, 0.46 g/L goethite, 0.01 M NaNO$_3$.

Metal complexation significantly affects the adsorption of chelating agents and both an increase and decrease in chelating agent adsorption have been observed in the presence of metal ions. Some studies for divalent metals (e.g. Zn, Cu, Co, Ni, Pb, and Ca) reported only a slight influence of the metals on NTA and EDTA adsorption onto oxides (*27, 37–40*). The fact that the identity of the metal was of little significance was interpreted as evidence that hydrogen bonds were responsible for the adsorption (*40*).

The structure of the chelate complex is also important in determining adsorption. A very strong influence of metals on EDTA adsorption is observed in the case of Co(II) versus Co(III) where Co(III)EDTA was adsorbed significantly less than Co(II)EDTA onto δ-Al$_2$O$_3$ (*34*). This was attributed to the differences in the stereochemistry of these chelates. Co(III)EDTA has a sexidentate configuration with all six coordinative positions of EDTA used for Co(III) complexation while Co(II)EDTA has a quinquedentate configuration. The carboxylate group not coordinated to the metal center is free for coordination to the surface. Differences in chelate complex structure were also used to explain the differences in adsorption of various metal–EDTA complexes on iron oxides (*31, 41*) (Figure 2). Complexes with the same structure in solution (e.g. Cd, Zn, Cu, Co(II), Ni, Pb) all have the same adsorption behavior. Complexes with the same charge but different structure, e.g. Pd(II)EDTA, have a completely different adsorption behavior. Adsorption of Pd(II)EDTA was much stronger than adsorption of other divalent metal complexes (*41*). Pd(II)EDTA has a bidentate structure compared to the other complexes that are quinquedentate (*42*). This shows clearly that it is not only the charge of the complex that determines the adsorption behavior but also the structure of the complex in solution.

Co(III)EDTA adsorption on goethite was very low and similar to Fe(III)EDTA and Cr(III)EDTA (*41*). But the adsorption of complexes with trivalent metals is not always weak, and adsorption was very strong for In(III)EDTA, Bi(III)EDTA, and La(III)EDTA, which do not have sexidentate structure (*42*)

The results from clean mineral phases can be transferred to natural adsorbents. Experiments conducted with a natural sand also showed that Co(II)EDTA and NiEDTA are much more strongly adsorbed than Co(III)EDTA (*43*, *44*). Adsorption of metal−EDTA complexes in a groundwater field test at pH 5−6 were found to be higher for NiEDTA than for Fe(III)EDTA (*45*), while on lake sediment at a pH of around 8, adsorption of Fe(III)EDTA was much higher than adsorption of NiEDTA and CuEDTA (*46*). Figure 2 shows that at low pH NiEDTA is more strongly adsorbed than Fe(III)EDTA, while at pH 8, however, adsorption of Fe(III)EDTA is stronger. The varying relative strength of adsorption of NiEDTA and Fe(III)EDTA in different environments can therefore easily be explained by the pH-dependence of the adsorption of the different complexes.

No data are available about the influence of metals on the adsorption of other aminopolycarboxylates. Adsorption of uncomplexed DTPA and HEDTA (hydroxyethylenediaminetetraacetic acid) on alumina was found to be very similar to that of EDTA, while adsorption of CDTA (diaminocyclohexanetetraacetic acid) was much stronger (*47*). It can be expected that the influence of metals on adsorption of these and other chelating agents is similar to that of EDTA and NTA.

Dissolution of Minerals. Dissolution of mineral phases by chelating agents can be attributed to ligand exchange reactions (*48*). The metal−oxygen bonds on the surface are weakened upon adsorption of the ligand, and the release of metal ions from the surface into the adjacent solution is enhanced. Chelating agents also increase the solubility of the metal in solution compared to the ligand-free system. This is especially important for iron oxides that have a very low solubility near neutral pH in the absence of ligands.

The dissolution of iron oxides by uncomplexed chelating agents, in particular EDTA, has been studied extensively (*49*−*52*). The rate of the ligand-promoted dissolution is related to the concentration of surface bound ligands. These investigations may be relevant for technical systems relating to the decontamination of metal surfaces but are only of limited value for assessing dissolution reactions in natural systems where the chelating agent is fully complexed by metals.

Figure 3 shows speciation calculations of EDTA in the presence of dissolved Zn with hydrous ferric oxide (HFO) as the solid phase, where both the complexation of EDTA by Zn and Fe(III) in solution and the solubility of HFO have been considered. Figure 3a shows that low pH favors formation of Fe(III)EDTA, while high pH favors formation of metal−EDTA complexes such as ZnEDTA. Addition of ZnEDTA to a HFO suspension at low pH therefore yields Fe(III)EDTA by a dissolution process. If the adsorption of the liberated metal onto the oxide surface (e.g. Zn^{2+} from ZnEDTA) is also taken into account, then the pH-range of Fe(III)EDTA stability is shifted toward higher pH values (Figure 3b). Partial formation of Fe(III)EDTA is therefore possible at pH values above 7.

Szecsody et al. (*53*) showed that metal−EDTA complexes are indeed able to dissolve iron oxides. They investigated the dissolution of iron oxide coated sand by Co(II)EDTA and CaEDTA and found that the formation of dissolved Fe(III)EDTA was proportional to the amount of adsorbed Co(II)EDTA and CaEDTA.

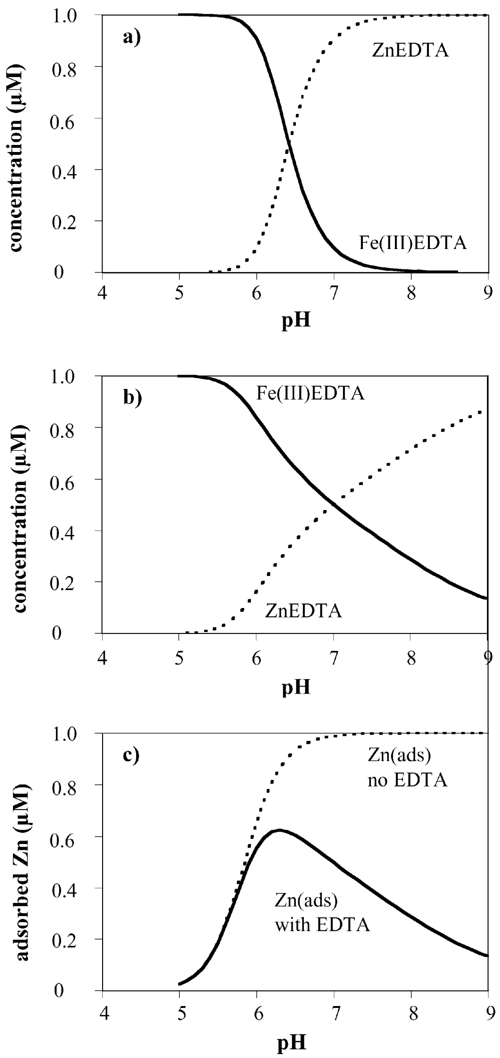

FIGURE 3. Speciation of a metal−EDTA complex in contact with an iron oxide is modified by dissolution and adsorption reactions. The figure shows the equilibrium speciation of EDTA in the presence of amorphous iron oxide (HFO) and Zn. (a) Concentration of Fe(III)EDTA in the presence of HFO without considering adsorption. (b) Fe(III)EDTA and ZnEDTA considering adsorption of Zn onto HFO. (c) Adsorbed Zn and ZnEDTA in the presence and absence of EDTA. All calculations assume 1 μM EDTA and Zn and 1 g/L HFO. The logK values for solution complexation were taken from ref *20*, for surface complexation from ref *30*.

Nowack and Sigg (*54*) investigated systematically the influence of complexation on the dissolution of iron oxides by metal−EDTA complexes. For HFO the rate decreased in the order EDTA ≫ CaEDTA > PbEDTA > ZnEDTA > CuEDTA > Co(II)EDTA ≫ NiEDTA. This sequence corresponds to the exchange kinetics of the metal−EDTA complexes (*18*) and indicates that dissociation of the surface ≡Fe-EDTA−metal complex is the rate-limiting step. For goethite, however, NiEDTA, CuEDTA, ZnEDTA, and PbEDTA had almost identical effects on the dissolution rates. In this case, the rate-limiting step is no longer the dissociation of the metal−EDTA complex but the detachment of iron from the goethite structure. Dissolution of amorphous iron oxide coatings and formation of Fe(III)EDTA in an aquifer was observed during a tracer test with ZnEDTA, CuEDTA, PbEDTA, and NiEDTA (*45*). The dissolution rate decreased in the order PbEDTA ≫ ZnEDTA > CuEDTA ≫ NiEDTA, the same as observed in the laboratory for HFO (*54*).

Although dissolution of iron oxides is the most important dissolution process in natural systems, other mineral phases can also be dissolved. SrEDTA and CdEDTA rapidly dissolved aluminum phases and dissolved AlEDTA was detected (*55*−*57*). Dissolution of Co(III)-oxides by EDTA, NTA, and IDA (iminodiacetic acid) resulted in the formation of dissolved Co(III)-complexes and reductive dissolution products (*58*).

Remobilization of Metals. Metals adsorbed onto a solid can be remobilized by chelates. Consequently EDTA and other chelating agents have been used for many years as extractants for metals from soils and sediments to characterize the plant available fraction (*59*). They have also been proposed as enhancers for the phytoremediation of heavy metals by plants (*60*−*62*) and for soil washing (*63*−*66*). In these systems very high concentrations of chelating agents are used. For an understanding of the potential risk of heavy metal mobilization by chelating agents at low concentrations, these investigations are only of limited value.

Speciation calculations can be used to predict the pH conditions that favor remobilization. Figure 3c shows Zn adsorption onto HFO in the absence and presence of EDTA as a function of pH. In the presence of EDTA, both Fe(III) from the dissolution of HFO and Zn compete for EDTA. At pH < 6, Fe(III)EDTA is the dominant species and consequently the influence of EDTA on Zn adsorption is negligible. At pH > 6, the Fe(III)EDTA concentration decreases (see Figure 3b) and EDTA can successfully compete with the surface for Zn. Addition of free EDTA or Fe(III)EDTA at high pH therefore results in a partial remobilization of Zn from the surface. In the reported remobilization studies (*5*, *63*, *66*−*71*) complexation with dissolved metals, dissolution of minerals (iron and aluminum oxides), and remobilization of adsorbed metals occurred simultaneously as predicted by the calculation. Theses studies also show that considering slow kinetics in addition to equilibrium consideration is very important.

The effect of the chelate speciation on heavy metal remobilization from oxides and sediments was investigated in detail (*72*). The remobilization of Zn from goethite at pH 8 was much faster with CaEDTA than with Fe(III)EDTA, reflecting the much slower dissociation kinetics of Fe(III)EDTA (*18*). Pb and Ni on the other hand were remobilized much faster with Fe(III)EDTA than with CaEDTA or ZnEDTA, which is in disagreement with the much slower dissociation kinetics of Fe(III)EDTA compared to CaEDTA. The rate-limiting step for this reaction is therefore not the dissociation of the metal−EDTA complex. More research is needed to further elucidate the surface chemistry of metal mobilization by ligands. EDTA was not able to remobilize Pb from HFO at pH 8 due to the very strong adsorption of Pb to the surface (*72*). Calculations have shown that at this pH Fe(III)EDTA is the prevalent EDTA species. The order of remobilization of Zn from a river sediment was CaEDTA > CuEDTA > Fe(III)EDTA, again in agreement with the dissociation rates of the metal−EDTA complexes (*18*).

Redox Reactions of the Coordinated Metal

A change in the oxidation state of the coordinated metal ions can completely change the behavior of the metal and of the chelate. The oxidation of Co(II)EDTA to Co(III)EDTA is of great importance because Co(III)EDTA is extremely stable. The stability constant for Co(III)EDTA (logK 39.8) increases by a factor of 10^{20} relative to Co(II)EDTA (logK 18.2). Co(III)EDTA exhibits only very weak interaction with surfaces (*34*, *43*, *44*) and is therefore rather mobile in the groundwater compared to Co(II)EDTA or aqueous Co(II).

Oxidation of Co(II)EDTA by O_2 is very slow (*43*). Manganese oxides, however, rapidly oxidize Co(II)EDTA to Co(III)EDTA (*55*, *56*, *73*). The proposed reaction elucidated by XANES spectroscopy, which is compatible with the lack of observed formation of Mn(II), is (*74*):

$$2\mathrm{MnO_2} + 2\mathrm{Co(II)EDTA}^{2-} + \mathrm{H_2O} \rightarrow \alpha\text{-}\mathrm{Mn_2O_3} + 2\mathrm{Co(III)EDTA}^{-} + 2\mathrm{OH}^{-} \quad (5)$$

The kinetics of Co(II)EDTA oxidation are dependent on MnO_2 surface regeneration under oxic conditions because the formed Mn(III)-layer oxidized Co(II)EDTA much more slowly than the Mn(IV) bearing parent material:

$$2\alpha\text{-}\mathrm{Mn_2O_3} + 2\mathrm{Co(II)EDTA}^{2-} + 6\mathrm{H}^{+} \rightarrow 2\mathrm{Mn}^{2+} + 2\mathrm{Co(III)EDTA}^{-} + 3\mathrm{H_2O} \quad (6)$$

This reaction may explain the observed Mn(II) in the column effluent in other investigations (*55*, *56*). Subsurface materials, which are very low in extractable Mn, do not exhibit significant oxidation of Co(II)EDTA (*43*).

Oxidation of Co(II)EDTA to Co(III)EDTA by Fe(III) was also observed in columns with iron oxide coated quartz (*44*) and in goethite suspension (*75*). In the presence of oxygen, the formed Fe(II) was rapidly reoxidized to Fe(III) and the surface was regenerated. Fe(II)EDTA is extremely rapidly oxidized to Fe(III)EDTA by molecular oxygen even at pH 3 (*76*, *77*). In the absence of oxygen, oxidation of Co(II)EDTA was also observed, although at a slower rate. A steady decline in the oxidation rate was observed due to the lack of regeneration of the reactive sites.

Reduction of chelated metals has also been observed. The iron-reducing bacterium Shewanella alga and the sulfate-reducing bacterium *Desulfovibrio vulgaris* can use Co(III)EDTA as a terminal electron acceptor, reducing it to Co(II)EDTA (*78*−*81*). Sulfide reduces Co(III)EDTA in a pathway involving polysulfide formation that leads to a Co(II)S precipitate (*81*).

Degradation

Photodegradation. Fe(III) and Cu(II) complexes of aminopolycarboxylates such as EDTA, NTA, DTPA, and EDDS are rapidly photodegraded (*82*−*85*), while most other complexes are not or only slightly photosensitive (*86*, *87*). Uncomplexed EDTA becomes photolabile upon sorption to the iron oxide lepidocrocite (γ-FeOOH) (*88*). Fe(III)EDTA is degraded in a stepwise process under successive decarboxylation (where ED3A is ethylenediaminetriacetate, EDDA ethylenediaminediacetate, and EDMA ethylenediaminemonoacetate) (*87*):

$$\mathrm{Fe(III)EDTA} \rightarrow \mathrm{Fe(II)ED3A} + \mathrm{CO_2} + \mathrm{HCOH} \quad (7)$$

$$\mathrm{Fe(III)ED3A} \rightarrow \mathrm{Fe(II)EDDA} + \mathrm{CO_2} + \mathrm{HCOH} \quad (8)$$

$$\mathrm{Fe(III)EDDA} \rightarrow \mathrm{Fe(II)EDMA} + \mathrm{CO_2} + \mathrm{HCOH} \quad (9)$$

The formed Fe(II)-complexes are rapidly oxidized to Fe(III)-complexes in the presence of oxygen. The final product EDMA is stable in the presence of Fe(III) and light (*89*). The photodegradation products of Fe(III)EDTA are readily biodegradable (*90*) compared to the recalcitrant parent compound.

For an evaluation of the observed concentration of EDTA in surface waters it is essential to know the fraction of EDTA species present as Fe(III)EDTA (*91*). The rapid photodegradation of Fe(III)EDTA results in a mean half-life of EDTA in river water of a few hours during summer and several days in winter (*92*, *93*). All other EDTA-species present in the river water are stable in the presence of light (*19*).

Chemical Degradation. Chelating agents are selected so that the corresponding metal ion complexes are stable during the technical operation under consideration. Breakdown typically requires longer time scales, more severe chemical conditions, or the presence of catalysts. Hydrolysis of free EDTA via C−N fission requires temperatures in excess of 175 °C (*94*). Rates of EDTA hydrolysis in the presence of divalent metal ions decrease in the order Mg > Ca > Zn > Fe > Ni, reflecting increasing percentages of total EDTA complexed by the added metal ion (*95*). In a similar manner, rates of NTA degradation at high temperatures decrease as the extent of complexation by divalent metal ions is increased (*96*). Breakdown of EDTA, NTA, and HEDTA (hydroxyethylenediaminetetraacetate) at room temperature was found in aqueous samples containing a complex mixture of Al, Fe(III), Cr(III), La(III), Nd(III), Mn(II), Ni, Zn, Cu(II), and Ca (*97*). At least 20 different breakdown products were identified. A number of metal ions included in this mixture have never been investigated in single metal ion experiments. Thus, there is no way to establish which free metal ion or chelate complexes caused chelating agent breakdown. Higher-valent metal ions may induce oxidation−reduction pathways for chelate breakdown. At 100 °C, Fe(III) is able to oxidize EDTA (*98*). Mn(III) is a far stronger oxidant than Fe(III) in a thermodynamic sense, and indeed the Mn(III)-containing mineral manganite (MnOOH) has been found to oxidize EDTA at room temperature with concomitant formation of Mn(II) (*58*, *99*). Mn(III)EDTA complexes decompose rather rapidly in aqueous solution with a pH-dependent rate (*100*, *101*). The reaction of Co(III)OOH with EDTA and NTA yields dissolved Co(III) species as ligand-assisted dissolution products and Co(II) and products of oxidative dealkylation as reductive dissolution products (*58*).

An interesting degradation pathway for chelating agents is the Mn(II)-catalyzed oxidation in the presence of molecular oxygen (*102*, *103*). The half-life for the reaction of nitrilotrismethylenephosphonic acid (NTMP), the phosphonate-containing analogue to NTA, in the presence of equimolar Mn(II) and in equilibrium with 0.21 atm O_2 is 10 min at pH 6.5, with the reaction occurring more slowly under more alkaline or acidic pH values. The presence of other cations such as Ca, Zn, and Cu(II) can considerably slow the reaction by competing with Mn(II) for NTMP. Catalytic Mn(II) is regenerated in cyclic fashion as the reaction takes place. Manganese-catalyzed oxidation of chelating agents is likely to be an important degradation mechanism in natural waters.

Reactive Transport

The transport of radionuclides and toxic metals from Department of Energy facilities throughout the United States is a threat to many groundwaters. EDTA and radionuclides have been codisposed at these sites, and the transport of ^{60}Co(II)EDTA and ^{60}Co(III)EDTA has received considerable interest (*104*).

The first paper by Jardine and co-workers on this topic (*55*) showed that displacement of the complexed metal by aluminum and iron oxides and the MnO_2-mediated oxidation of Co(II)EDTA were the most important reactions affecting the speciation and transport of EDTA. The oxidation reaction was studied in detail in column experiments with MnO_2-coated silica (*73*) and with undisturbed subsurface material (*57*). In subsurface material containing no manganese oxides, transport of Co(II)EDTA is affected by its oxidation to Co(III)EDTA by Fe(III) oxides (*44, 105*). Transport of complexes such as CdEDTA or SrEDTA that do not undergo redox reactions is influenced by ligand-promoted dissolution of aluminum and iron oxides and formation of AlEDTA and Fe(III)EDTA (*55, 57*). The picture is further complicated because bacterial reduction of Co(III)EDTA formed by oxidation of Co(II)EDTA also occurs (*80*). Also in Fe-reducing environments, surface interactions of Co(II)EDTA and CdEDTA with biotite yielded significant concentrations of Fe(III)EDTA (*106*).

The reactive transport of EDTA is therefore affected by sorption, redox and dissociation reactions. Mathematical models have been developed that are able to accurately describe transport and speciation of EDTA in the column (*107*, *108*).

Not only Co(II)EDTA but also other metal−EDTA complexes were studied in the field. The transport of PbEDTA, ZnEDTA, CuEDTA, and NiEDTA was followed in a sandy aquifer (*45*, *109*−*111*). Ligand-promoted, species-dependent dissolution of iron oxides and formation of Fe(III)EDTA was the process determining EDTA speciation. The changes in speciation of EDTA infiltrating from river water to groundwater have also been followed (*112*). The Fe(III)EDTA fraction decreased from 35% in the river to 11% of total EDTA in the groundwater 16 m away from the river. Exchange of Fe(III)EDTA with dissolved metals and remobilization of adsorbed metals, e.g. Zn, have rapidly changed EDTA speciation.

Speciation

Analytical Techniques. Numerous methods are available for total EDTA, NTA, and DTPA analysis in natural samples (*113*). While gas chromatography has been used for many years as a standard method, it has recently been replaced by high performance liquid chromatography. The principle of most HPLC methods is the precolumn complexation of the chelating agents by Cu(II) or Fe(III), separation of the complexes as ion-pairs on a reversed-phase column, and detection by UV or visible-absorption of the colored complexes (*114*−*120*).

The same analytical methods are also able to separate different metal-complexes, but the detection limits are quite high. Separation and direct detection of Mn(II)EDTA, ZnEDTA, and CuEDTA by HPLC (*121*−*124*) and of Co(II)EDTA and Co(III)EDTA by ion chromatography (*125*) have been described. The latter method has been used to investigate the oxidation of Co(II)EDTA in column experiments (*43*, *44*, *56*, *73*). Using a fluorescent postcolumn derivatization, similar detection limits have been achieved for the EDTA complexes of Pb, Zn, Cu, and Cd (*126*). Capillary electrophoresis has been applied to detect metal−DTPA (*127*), metal−EDTA (*128*, *129*), NiEDTA (*130*), and metal−NTA complexes (*131*). Metal−EDTA complexes can also be quantified directly by electrospray without previous chromatographic separation (*132*). Metal−EDTA complexes have been measured with detection limits of 0.1−1 μM using ion-chromatography-electrospray mass spectrometry (*133*). Due to the high detection limits none of the methods mentioned above has been used to determine the speciation in natural waters.

Further improvements of HPLC methods made it possible to detect EDTA complexes of Cd, Co(II), Cu(II), Pb, and Zn in wastewater with a detection limit of less than 0.1 μM (*134*). For example, 300 nM CuEDTA and ZnEDTA were directly detected in the effluent from a wastewater treatment plant.

Fe(III)EDTA can be determined in water samples by illumination of a sample, which results in the complete and selective photodegradation of only Fe(III)EDTA (*19*, *91*). Using this procedure it has been shown that Fe(III)EDTA is a major EDTA-species in wastewater (*19*) and natural waters (*91*). NiEDTA can be quantified by methods that use precolumn formation of Fe(III)EDTA (*118*, *135*, *136*). NiEDTA reacts only slowly with Fe(III), necessitating heating to 90 °C for 3 h for a complete formation of Fe(III)EDTA. Eliminating the heating step will prevent the conversion of NiEDTA to Fe(III)EDTA. NiEDTA has been detected by this method in wastewaters (*118*, *135*, *136*), with a maximum amount of 42% of total EDTA (*135*).

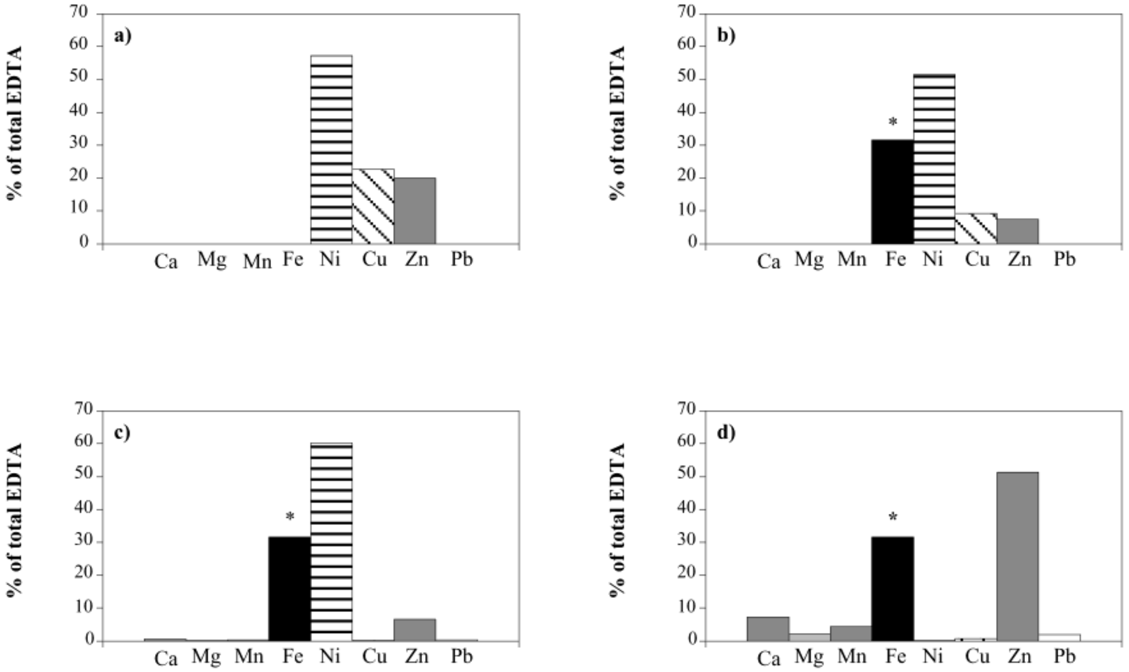

FIGURE 4. The calculated species distribution of a chelating agent is determined by the complexity of the system. The example shows the speciation of EDTA in a river water determined by a combination of analytical methods and equilibrium calculations. (a) Total concentrations of metals, EDTA, and NTA. (b) Fe(III)EDTA measured, otherwise as in (a). (c) Natural ligands for Cu and Zn included. (d) Natural ligands for Ni included. (*) indicates a measured concentration that was fixed at this value. Total EDTA 43 nM, total NTA 8.7 nM. Data from ref *112*.

Recently a very promising chromatographic method has been reported for the determination of the speciation of chelates at trace concentrations (*137*, *138*). The method uses anion-chromatography coupled to ICP/MS for selective determination of metal complexes. The method can determine the metal complexes of various chelates such as NTA, EDTA, DTPA, and EDDS at concentrations of a few nM. This method will definitely be of invaluable help for all further speciation studies.

Speciation Calculations. Because no trace analytical method was available to determine the chelate species in natural waters, speciation calculations have been repeatedly used. For example it was calculated that CuNTA and NiNTA should be the major NTA species in a river water (*3*, *13*, *139*). The dominant EDTA species in the environment have been proposed to be CuEDTA and, at low pH, Fe(III)EDTA (*140*). Equilibrium calculations have also been combined with titration curves of river water samples (*141*, *142*). CuEDTA was found to be between 45 and 98% of total EDTA, Fe(III)EDTA between 2 and 50%, NiEDTA between 0 and 33%, and ZnEDTA between 2 and 31%.

Most of these calculations omit that besides the chelate of interest, other chelates and natural ligands are present in the water that compete for the available metals. Sigg and Xue (*143*) have shown that considering the natural ligands for Cu and Zn is critical for obtaining an accurate speciation of EDTA and NTA. Calculations involving natural ligands have been performed to determine the speciation of [S,S]-EDDS in natural waters (*144*).

In the following section an example is presented based on literature data (*112*) to show how the determination of the speciation of EDTA and NTA in a river depends on the complexity of the system. The example may be representative for a river with moderate anthropogenic metal pollution.

In a first step, the total concentrations of EDTA and NTA and of the metals in filtered river water were considered, which is the commonly used approach. EDTA was calculated to be present as 57% NiEDTA, 20% ZnEDTA, and 23% CuEDTA (Figure 4a). This result is in good agreement with literature data cited in the preceding section. Fe(III)EDTA is not expected to be present at significant concentrations in the sample due to the rather high pH of 8.1. The exchange reactions of Fe(III)EDTA are, however, very slow and equilibrium cannot be assumed (*18*). A direct measurement of Fe(III)EDTA revealed that 32% of the total EDTA was present as Fe(III)EDTA. Its concentration is determined by the amount of Fe(III)EDTA released by wastewater treatment plants (*19*) and by the photochemical degradation of Fe(III)EDTA in the river (*91*). The only way to establish this fraction was by measurement.

In Figure 4b the fraction of Fe(III)EDTA was set at the measured value and only the speciation of the remaining EDTA was calculated. The result is not very different from Figure 4a and 51% NiEDTA, 32% Fe(III)EDTA, 9% CuEDTA, and 7% ZnEDTA are the most important species.

River waters not only contain EDTA and NTA but also strong natural ligands for metals such as Cu (*145*), Zn (*146*), and Ni (*147*). These ligands compete with EDTA and NTA for the same metals and have to be included in speciation calculations. While the chemical identity of these ligands is still unclear (*148*), they can clearly be linked to biological activity (*149*). When we included the concentrations and stability constants of the natural ligands for Cu and Zn in the speciation model, the species distribution was 60% NiEDTA, 32% Fe(III)EDTA, and 7% ZnEDTA (Figure 4c). CuEDTA was less than 0.1% of total EDTA because the very strong natural ligands compete successfully for Cu in the sample. As a result, the calculation predicted that almost all EDTA (except Fe(III)EDTA) was bound to Ni. Measurements have shown, however, that NiEDTA was less than 5% of total EDTA in the sample (*112*). Natural ligands for Ni were not measured in the sample, but recently concentrations and stability constants of natural Ni ligands have been reported for the same sampling location (*147*). When these ligands were included in our calculation the species distribution shown in Figure 4d was obtained. NiEDTA almost completely disappeared because the natural ligands were stronger chelates for this metal than EDTA. The most important EDTA species were now ZnEDTA with 51%, Fe(III)EDTA with 32%, CaEDTA with 7%, and Mn(II)EDTA with 5%. CuEDTA was only 0.8% and NiEDTA less than 0.1%, reflecting the large binding constants of the natural ligands for these metals.

These calculations show that for assessing the speciation of chelates in the environment, the natural ligands for Cu, Zn, and Ni have to be considered, otherwise an incorrect speciation will be obtained. For example, a comparison of parts a and d of Figure 4 reveals no similarities between the two species distributions. Only an analytical method able to speciate EDTA at low concentrations in natural samples can show whether the result presented in Figure 4d represents the actual species distribution.

The speciation of NTA was also calculated using the same methods described above for EDTA. For NTA the speciation changed even more dramatically with increasing complexity of the system. When only the total concentrations were considered, speciation calculations predicted CuNTA (51%), ZnNTA (35%), and NiNTA (6%). When all natural ligands and EDTA were also considered, speciation calculations predicted CaNTA (62%), MgNTA (29%), free NTA (5%), and ZnEDTA (3%). NTA may therefore be considered almost exclusively coordinated to alkaline earth metals due to their higher concentration in natural waters. Only in soft waters may complexation of Ni and Zn be of importance for NTA speciation.

The use of the newly developed HPLC-ICP/MS method (*137*, *138*) is expected to provide urgently needed measurements of the actual speciation of the chelating agents in the environment, which can then be used as the basis for a refined risk assessment of aminocarboxylates in natural waters.

Future measurements should also include other chelating agents besides EDTA and NTA that are used in high quantities. The detection of PDTA (propylenediaminetetraacetic acid) at concentrations equivalent to NTA has been reported for German rivers (*150*). Additionally, breakdown products of EDTA and DTPA have been detected at concentrations equal to the parent compound (*151*). These breakdown products are still chelating agents and have to be included in the assessment of the effects of the parent compounds EDTA and DTPA. Phosphonic acids are a group of chelating agents that are used in large amounts and have been detected in wastewater (*152*) but have never been measured in natural waters. The discussion of chelates in natural waters and their effect on metal speciation should include all these compounds. To date, the focus has been mainly set on EDTA and NTA and has largely ignored the presence of other chelating agents.

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